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Investigation of ZnO nanostructures synthesized from different zinc salts

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Abstract : This article reports the synthesis of ZnO nanostructures and its characterization by hydrothermal method. Different zinc salts such as zinc nitrate, zinc acetate and zinc sulfate are used as regents for the growth of ZnO nanostructures. The effect of counter ions (NO₃⁻, CH₃COO⁻ and SO₄⁻²⁻) on the structural, morphological and optical properties is investigated. The different counter ions show the effect on the morphology of ZnO samples, in turn cause the different optical emission properties. X-ray diffraction (XRD) patterns indicate that ZnO nanostructures possess the hexagonal wurtzite structure and ûne crystalline size, regardless of the counter ions. Scanning electron microscopy (SEM) and trans-

INTRODUCTION

Zinc oxide (ZnO) nanostructures have attracted great interest because of their unique optoelectronic properties and various applications in sensors, solar cells, electrochemical cells and flat panel displays etc^[1-6]. ZnO has rich family of nanostructures and its properties directly depend on the microstructures of the materials such as orientation, crystal size, mission electron microscopy (TEM) images show that various morphologies such as nanoflowers, nanoflakes and nanoprisms are obtained from zinc nitrate, zinc acetate and zinc sulfate precursors, respectively. The spectra of photoluminescence and Raman show ZnO nanostructures synthesized from various precursors have different intensity of emission bands, which shows the presence of various crystal defects and oxygen vacancies in the samples. © **Global Scientific Inc.**

Keywords : ZnO nanostructures; Hydrothermal method; Zinc salts; Optical properties.

morphology, as well as aspect ratio. Since the microstructures strongly affect the optoelectronic properties of ZnO, it is highly desired to control the morphology of ZnO nanostructures for its effective application. Great efforts have been paid to control the size and shape of ZnO nanomaterials^[5-8]. In the process of ZnO nanostructurs synthesis, the morphology of ZnO is affected by many factors, such as synthesis methods, synthesis technology, synthesis pre-

cursors etc^[9-13].

92

The commonly used precursors for the synthesis of ZnO nanomaterials are zinc nitrate, zinc acetate and zinc sulfate. Different kinds of anionic species in the solutions have different nucleation and growth kinetics, which can greatly influence the growth manner, size, crystallographic and the morphology of the ZnO and their properties. However, most previous studies only used a single zinc salt, and the influences of different anonic species from starting materials on the morphology and structure of the obtained ZnO nanostructures is less studied.

Hydrothermal method is an important technology in synthetic material. By using this method, one can get completely developed crystal grains with uniform size. In this work, we reported the effects of different precursors such as zinc acetate, zinc nitrate, as well as zinc sulfate on the morphology and optoelectronic characteristics of ZnO nanostructures synthesized by hydrothermal method, and analyzed the causes of these results.

EXPERIMENTAL

Materials

Zinc nitrate hexahydrate $(Zn(NO_3)_2 \cdot 6H_2O, \ge 98\%)$, zinc acetate dihydrate $(Zn(CH_3COO)_2 \cdot 2H_2O, \ge 99\%)$, zinc sulfate heptahydrate $(ZnSO_4 \cdot 7H_2O, \ge 99.5\%)$, potassium hydroxide (KOH, $\ge 98\%$,) were used as received. All the reagents were analytically pure and used without further purification. Distilled water was used throughout the experiment.

Synthesis

Synthesis of zinc oxide nanoparticles from zinc nitrate

In this experiment, 40 mL of 0.04 M Zn $(NO_3)_2$ solution was added into 40 mL of 0.16 M KOH solution. The mixture was sonicated for 30 min, and then sealed into a Teflon-lined stainless-steel autoclave. The autoclave was heated at 120 °C for 3 h and then cooled down to room temperature naturally. The precipitate generated by chemical reaction was centrifuged and washed with distilled water and ethanol three times, and dried at 70 °C in air.

Synthesis of zinc oxide nanoparticles from zinc acetate

ZnO nanoparticles from zinc acetate were synthesized by using the same process as mentioned above. The only difference was that Zn $(NO_3)_2$ solution was altered to 0.04 M Zn $(CH_3COO)_2$ solution.

Synthesis of zinc nanoparticles from zinc sulfate

ZnO nanoparticles from zinc sulfate were synthesized by using the same process as mentioned above. The only difference was that 0.04 M Zn $(CH_3COO)_2$ solution was altered to 0.04 M ZnSO₄ solution.

Characterization

The x-ray diffraction (XRD) pattern was measured by X' PertPRo diffractometer (PANalytical) with parameters of step = 0.02, time/step = 5 s, and the same slits for the two samples. The target is Cu $K\alpha$ ($\lambda = 1.54$ Å), with the power of 30 kV × 30 mA. he scan rate was fixed at 0.1°/s in order to record the XRD patterns for the 2θ range of 30° "80°. The surface morphology of the samples was studied by using scanning electron microscopy (SEM) (SEM, LEO 1530 VP). Transmission electron microscopy (TEM) images were obtained by using a JEOL 2010H microscope (TEM) operating at 100 kV. The samples for TEM analysis were prepared by dropping dilute ethanol solutions of ZnO nanocrystals onto carbon-coated copper grids. Photoluminescence spectra (PL) of ZnO samples for the measurement of optical properties were taken using a fluorometer (JY FL-3), instrument with 450 W Xenon lamp source and 325 nm excitation wavelength and recorded the curves in the region of 350~600 nm. Raman spectrum was measured at room temperature by using Ar⁺-ion laser (488 nm) as the excitation source on a commercial scanning near-ûeld optical microscope (Alpha SNOM, WITec).

RESULTS AND DISCUSSIONS

The results from XRD

Figure 1 shows that the X-ray diffraction patterns of ZnO nanostructures synthesized from zinc nitrate, zinc acetate, and zinc sulphate. All the



Figure 1 : X-ray diffraction patterns of ZnO nanostructures synthesized from different zinc salts

samples have same 2θ values of peaks at 31.75° , 34.4° , 36.24° , 47.48° , 56.56° , 62.76° , 66.32° , 67.96° , 69.16° , 72.6° , and 77° , corresponding to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) planes of ZnO, respectively. The samples can be directly indexed to the hexagonal wurtzite structure irrespective of counter ions, and the lattice parameters are a = b = 0.3254 nm, c = 0.521 nm, which agrees well with JCPDS card no. 36-1451. There are no other diffraction peaks detected, indicating that the synthesized ZnO samples have high purity.

Growth mechanisms and morphology

Generally, the formation process of ZnO nanocrystals can be divided into two stages: crystal nuclei and crystal growth. The reaction for the growth of ZnO nanocrystals may be described as follows^[14]. $Tn^{2}+2OH \rightarrow Zn(OH)$ (1)

	(1)
$\operatorname{Zn}(\operatorname{OH})_2 + 2\operatorname{OH}^{-} \leftrightarrow [\operatorname{Zn}(\operatorname{OH})_4]^2$	(2)

$[Zn(OH)_4]^2 \leftrightarrow ZnO+2OH^2+2H_2O$ (3) At the beginning of this process the white

At the beginning of this process the write $Zn(OH)_2$ precipitates is obtained[see reactions (1)]. Next, as the KOH is added into the Zn^{2+} aqueous solution, some of the OH⁻ ions in the solution may react with $Zn(OH)_2$ precipitates, resulting in an agglomerate with the form of[$Zn(OH)_4$]²⁻[see reactions (2)]. Finally, a large number of ZnO nuclei form from the dehydration of[$Zn(OH)_4$]²⁻ when the concentrations of Zn^{2+} and OH⁻ ions exceed the critical value, and a subsequent crystal growth process develops[see reactions (3)].

ORIGINAL ARTICLE



Figure 2 : SEM images of ZnO nanostructures synthesized from different zinc salts: (a) zinc nitrate, (b)zinc acetate, (c)zinc sulfate

Figure 2 presents the SEM images of ZnO nanostructures which were synthesized from different zinc salts. Obviously, the morphologies of these

94

samples are quite different from each other, suggesting that different counter ions play a key role in the different morphologies of ZnO nanostructures. Flower-like nanostructures consisting of many wellaligned nanopetals with an average length of 200 nm and a width of 100 nm in Figure 2(a) are obtained from zinc nitrate precursor. The microstructures are very similar to beautiful natural flowers. The radially oriented nanostructures are supposed to be the condensation of nanocrystallines. Due to the nitrate ion in the reaction system, when using KOH as mineralizer, there is no buffer reagent in the mixture so that the rate of growth increased compared to the acetate-KOH and sulfate-KOH systems. The environment of growth is relatively unstable, at the early reaction stage, ZnO spontaneously nucleates from the solution of $Zn(OH)_4^{2-}$ to multinuclei aggregates. As the reaction proceeding continues, these multinuclei aggregates can serve as the sites, in which each nucleu in the aggregate grows anisotropically along the[0001] direction to form the flower-like ZnO nanostructures.

Thin nanoflakes with average length of 300 nm and thickness of 50 nm in Figure 2(b) are obtained from zinc acetate precursor. It is suggested that acetate ion has a strong ability to connect with positively charged zinc atoms in the Zn enriched surface planes (1011) of the ZnO particles through the -COOand -OH groups, and suppress the growth along[0001] orientations. Acetate ion forms an amphiphilic capping layer which potentially prevents extensive fusion of the particles in the same way as citrates are used during the controlled growth of complex and oriented ZnO structures^[15].

Cone-shaped prisms in the Figure 2(c) are obtained from zinc sulfate precursor. The average dimensions of the observed ZnO are in the range of 50-200 nm. It is indicated that these prisms stem from the oriented self-assembly and condensation of the nanoprisms along the c-axis[0001]. Due to the strong alkaline solution, the dominant state of the deposited zinc hydroxide precursor is $Zn(OH)_4^{2-}$ specie, which is absorbed on the most positive surfaces (0001) of ZnO nucleus and continue to growing on the surface of ZnO. However, these growth units with negative charge repel each other in the case of excess absorption, the rate of (0001) surface slow. Then some growth units tend to the second positive or even third positive surfaces, so all surface has certain growth rates. Finally, zinc oxide forms as cone-shaped prisms.

From the above images, the morphologies of three samples are further characterized by TEM. Flowerlike nanoparticles, nanoflakes and amorphous particles are obtained from zinc nitrate precursor, zinc acetate precursor and zinc sulfate precursor, respectively. They all agree with the SEM images well. By comparing the SEM images in Figure 3, it is found that the sample synthesized from zinc nitrate are composed of small nanoparticles[Figure 3(a)], which aggregates to pieces of petals. The rode-like thing synthesized from zinc acetate in Figure 3(b) is the nanoflake upright, not the nanorods. Figure 3(c) shows that the sample from zinc sulfate consists with small cone-shaped particles and small rods.

Figure 3(a) give the structure of a ZnO flower with a good shape, and the Figure 3(d) show one petal of it and the corresponding selective area electron diffraction (SAED) pattern of this individual petal. The TEM graph of the petal prove that the petal is not a single-crystal rod but an assembly of some particles with very small diameter. Correspondingly, the SAED pattern presented in Figure 3(d) is characterized by the symmetrical stripes, as we all known, indicating that in the petal there are some ordered arrangement of crystallites.

Photoluminescence of ZnO particles

The optical properties were identified by using PL spectra with an excitation wavelength of 325 nm. Figure 3 indicates that all samples show the same broad emission ranging from 360 nm to 560 nm. The emission peaks are at 396, 437, 486 and 522 nm, which belongs to the violet, blue and green region. But the intensity of emission bands is found to be different, and the order of PL spectral intensity of ZnO samples is noted to be in the order of nitrate < sulfate < acetate, which may be due to different counter ions resulting in different morphologies and optical properties. Although the origin of these emissions is still in controversy^[16], PL spectra of ZnO have been explained with various mechanisms. Com-



Figure 3 : TEM images of ZnO nanoparticles synthesized from different zinc salts: (a) zinc nitrate, (b) zinc acetate, (c) zinc sulfate

monly, the band-edge emission at 396 nm is attributed to the recombination of excitons, and the visible emission in ZnO is attributed to different intrinsic and surface defects^[16-20]. It has been reported that the PL spectral intensity specifies the content of surface oxygen vacancies and crystal defects of the sample. If the spectral intensity is higher, the sample may have high oxygen vacancies and defects^[21]. Moreover, the content of surface oxygen vacancies and defects in the sample decreases with increasing particle size. Therefore, ZnO nanostructures synthesized from zinc nitrate show lower intensity of PL spectrum, which is due to the large particle size and fewer oxygen vacancies and defects. However, ZnO sample synthesized from zinc acetate possesses smaller particle size as seen from the SEM and TEM images, so that it has more oxygen vacancies and defects, and its intensity of PL spectrum is higher.

Raman spectra of ZnO samples

Raman spectra are known to be an effective technique for investigating the crystallization, structure and defects in nanostructure materials. According to the group theory, hexagonal wurtzite ZnO belongs to the C_{6v}^{4} space group, and exists the optic modes Γ_{opt} = $A_1 + 2B_1 + E_1 + 2E_{2l} + 2E_{2l}$



Figure 4 : TEM micrographs of flowerlike ZnO nanostructures: (a) the tip structure of one petal and its SAED pattern

lar modes and are Raman active, whereas the B_1 modes are Raman inactive (silent modes). The two non-polar E_2 modes (E_2 (low) and E_2 (high)) are also Raman active. Moreover, A_1 and E_1 modes can split into transverse optical (TO) and longitudinal optical (LO) phonons. Figure 5 shows the Raman spectra of ZnO samples from different zinc salt precursors. The Raman spectra curves of ZnO nanostructures from zinc nitrate precursor and zinc sulfate precursor are almost the same. The peaks are at 201, 331, 382, 438, 533, 584, 663, 1105, and 1153 cm⁻¹. The peak of ZnO nanostructures from zinc not substructures from zinc nanostructures from zinc nanostru

The characteristic wurtzite E_{2} (high) mode at 438 cm⁻¹ is observed in all these samples, which conforms the characteristic peak of the hexagonal wurtzite phase and crystal quality^[25]. The peak at 382 cm⁻¹ corresponds to transversal optical mode with A₁ symmetry, The peaks at 201, 331, 533 and 1030-1200 cm⁻¹ correspond to the second order Raman scattering, which arises from zone-boundary phonon scattering^[26,27]. The peak at 584 cm⁻¹ corresponds to longitudinal optical LO modes with E₁ symmetry. No Raman peaks related to impurity phases are observed, which confirms the pure wurtzite phases in the ZnO samples. A remarkable high Raman intensity of ZnO nanostructures from nitrate precursor is observed, which also further shows ZnO samples from zinc nitrate with larger particle sizes possess fewer oxygen vacancies and defects.



Figure 5 : PL spectra of the three samples synthesized from different zinc salts.

The results here are quite well consistent with that found in PL spectra.

CONCLUSION

In summary, a hydrothermal method has been adopted to synthesize ZnO samples by using zinc nitrate, zinc acetate and zinc sulfate as precursors. Different nanostructures were obtained, such as nanoflowers, nanoflakes and nanoprisms. The different counterions show an important influence on the morphology, crystal quality and optical properties of synthetic ZnO samples. The results show ZnO samples from zinc nitrate with larger particle sizes possess fewer oxygen vacancies and defects, while acetate sample with smaller particle sizes has more oxygen vacancies and defects. We also analyze the causes of these results.

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